Öğüt, Chelikowsky, and Louie Reply: In their Comment on our Letter [1], Franceschetti, Wang, and Zunger (FWZ) try to interpret our *ab initio quantum mechanical calculations* on Si nanocrystals in terms of *classical electrostatics* and the *effective mass approximation* (EMA) using *ad hoc* empirical adjustments [2]. Such an interpretation is done to show that our *ab initio* calculations for the optical gaps of Si nanocrystals are consistent with their *empirical* calculations. To achieve this consistency, FWZ claim that *two* adjustments need to be included in our expression for the optical gap. Here, we show that such a mixture of quantum mechanical and classical approaches for microscopic properties of nanocrystals is misleading, and leads to unphysical material properties.

The calculation of the optical excitation energy $\varepsilon_g^{\text{opt}}$ in a nanocrystal is inherently a quantum mechanical problem, which requires handling the well-defined components comprising this energy (quasiparticle energy $\varepsilon_g^{\text{qp}}$ and exciton Coulomb energy E_{Coul}) at the microscopic level. The quantum mechanical expression for $\varepsilon_g^{\text{opt}} = \varepsilon_g^{\text{qp}} - E_{\text{Coul}}$ in an n-electron nanocrystal *is* given in terms of the total energies E of n-, $(n+1)$-, $(n-1)$-electron systems, the electron and hole wave functions, and the microscopic dielectric screening function $\epsilon(\mathbf{r}_1, \mathbf{r}_2)$ as

$$\varepsilon_g^{\text{opt}} = [E(n+1) + E(n-1) - 2E(n)]$$
$$- \int \int \frac{|\psi_e(\mathbf{r}_1)|^2 |\psi_h(\mathbf{r}_2)|^2}{\epsilon(\mathbf{r}_1, \mathbf{r}_2)\,|\mathbf{r}_1 - \mathbf{r}_2|}\, d\mathbf{r}_1 d\mathbf{r}_2. \quad (1)$$

$\varepsilon_g^{\text{opt}}$ can be interpreted as the energy needed to create a noninteracting electron-hole pair, minus the exciton binding energy due to the Coulomb interaction. In our paper [1], all terms included in Eq. (1), with the exception of an approximation to $\epsilon(\mathbf{r}_1, \mathbf{r}_2)$, are calculated *ab initio*, while FWZ have calculated $\varepsilon_g^{\text{opt}}$ using an empirical approach from what they call the "standard equation" as $\varepsilon_g - E_{\text{Coul}}$ [Eq. (1) of the Comment]. *There is nothing standard about the "single-particle" gap ε_g in this equation.* It results from fitting bulk interaction parameters and postulating their transferability to the nanocrystalline environment. The inability inherent in an empirical pseudopotential to respond self-consistently down to sizes of 2–3 nm has been noted by one of the authors of the Comment [3]. Unlike the $\varepsilon_g^{\text{qp}}$ defined to be the difference between the ionization energy and the electron affinity, ε_g *is not a physically meaningful quantity, and can take on any value depending on the method employed.* For example, within density functional theory, different Kohn-Sham formulations can yield significantly different ε_g's [4]. Furthermore, of the two adjustments that FWZ claim should be included in our expression for $\varepsilon_g^{\text{opt}}$, the first one, i.e., $-E_{\text{pol}}^{eh} = -(e^2/R)(1/\epsilon_{\text{out}} - 1/\epsilon_{\text{in}})$, *does not exist* in the correct quantum mechanical expression [Eq. (1)]. The formulas for Σ_{pol} and E_{pol}^{eh} used in the Comment, although claimed to be "rigorous," result from treating a *macro-scopic* object with a *fixed* dielectric constant ϵ_{in} inside a medium of ϵ_{out} using classical electrostatics and EMA. The inability of EMA to reproduce quantum mechanical results has also been noted in earlier papers by FWZ [5]. Hence, we see no microscopic reason for using classical electrostatics coupled with EMA to establish a consistency between *ab initio* and empirical calculations. Any agreement established in this fashion [Fig. 1(a) of the Comment] is likely to be a fortuitous coincidence. Equation (1) *will* yield the correct $\varepsilon_g^{\text{opt}}$ with the correct $\epsilon(\mathbf{r}_1, \mathbf{r}_2)$, for which our paper provides an *improved distance-dependent* approximation. There is no quantum mechanical principle for introducing an extra classical term, such as E_{pol}^{eh}, as claimed by FWZ.

The second adjustment claimed implicitly by FWZ (in the figure caption) is the addition of a 0.68 eV self-energy correction to our $\varepsilon_g^{\text{qp}}$. We disagree with this claim, which has already been addressed by us in Ref. [6]. Here, we present additional evidence supporting our arguments. If the extra 0.68 eV were to be added to our calculated $\varepsilon_g^{\text{qp}}$, our E_{Coul} values would have to be increased by approximately the same amount to achieve good agreement with experiment. This would result in very large (≈ 1.1 eV) *screened* Coulomb energies $E_{\text{Coul}}^{\text{scr}}$ for nanocrystals of 2.3–3 nm in diameter. If this were true, it would imply, using our *unscreened* Coulomb energies $E_{\text{Coul}}^{\text{unscr}}$ in Fig. 2 of Ref. [1], effective dielectric constants $\bar{\epsilon} = E_{\text{Coul}}^{\text{unscr}}/E_{\text{Coul}}^{\text{scr}}$ near 1.5. Such large $E_{\text{Coul}}^{\text{scr}}$'s implying such small $\bar{\epsilon}$'s are unrealistic for Si nanocrystals of 2.3 to 3 nm diameter. For example, Wang and Zunger's parametrization [5] results in $\bar{\epsilon} \approx 8.5$ in this size regime.

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